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Photoluminescent properties of polyoxyethylene alkyl ether-type neutral surfactant templated mesoporous materials CMI-1: The absence of the 1.9 eV PL band

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Abstract

The photoluminescent properties of a neutral surfactant templated highly ordered mesoporous silica CMI-1 have been studied and compared with those synthesized with cationic surfactant. The absence of the emission at 1.9 eV is for the first time observed and is quite important for opto-electronic nanocomposite preparation using CMI-1 as matrix. Also for the first time, the possible origin of the emission band at 3.89 eV is identified.

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1. Introduction

Mesoporous materials have extensively been used for their adsorptive and acido-basic properties in catalysis and separation processes. More recently, they have been used as matrix for the incorporation of a variety of guests, such as dye molecules [1], enzymes [2], polymers [3] and semiconductors [4] for advanced nanocomposites preparation [5]. The textural, structural, morphological and other characteristics, such as acidic properties and adsorptive capacities of mesoporous silicas were well known since their discovery in the 90s [6]. Unfortunately, few investigations on the optical properties of such materials have been performed. As their structure is made of amorphous silica walls, their photoluminescent characteristics could be expected to be similar to those of amorphous silica glass.

Photoluminescence of amorphous silica glass is usually dominated by the presence of structural defects in the silica framework, such as E' centers ($\equiv\text{Si}^\bullet$), non-bridging oxygen hole centers (NBOHC) ($\equiv\text{Si}-\text{O}^\bullet$), oxygen vacancies etc. (Table 1) [7–12]. In particular, the presence of a PL band at 1.9 eV due to NBOHC defect centers very often hinders preparation of optical materials from silica glasses. The elimination of this band, i.e. elimination of the non-bridging oxygen hole defects, is a great challenge to the preparation of transparent silica glasses.

The PL spectra of mesoporous materials like MCM-41, synthesized using a cationic CTMABr surfactant are quite different although the PL bands are supposed to be induced by the same structural defects as for silica glass [13]. It is well known that highly ordered mesoporous silicas can be synthesized by different pathways, i.e. electrostatic interaction or hydrogen bonding, depending on the inorganic source (I) and surfactant molecules (S): S^+I^- , S^-I^+ , $\text{S}^\circ\text{I}^\circ$, $(\text{S}^\circ\text{M}^+)\text{I}^-$, and also on the synthesis conditions. The different pathways can generate quite different surface properties, thus different structural defects. Mesoporous materials CMI-1 were synthesized via an assembly of

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Table 1
Position and assumed origin of structural defects generally encountered in the framework of silica glass [7–12]

Position	Origin
1.9 eV	Non-bridging oxygen hole centers (NBOHC) ($\equiv\text{Si}-\text{O}^\bullet$)
2.7 and 4.3 eV	E' centers ($\equiv\text{Si}^\bullet$)

decaoxyethylene cetyl ether and tetramethoxysilane (TMOS) on the basis of hydrogen bonding [14].

The present Letter deals with the photoluminescence properties of mesoporous materials CMI-1 to study the effect of the different synthesis pathways on the optical properties of mesoporous silicas. The results obtained can help furthermore to better understand the surface properties induced by using different surfactant molecules.

2. Experimental

2.1. Mesoporous CMI-1 materials synthesis

A micellar solution of decaoxyethylene cetyl ether [$\text{C}_{16}(\text{EO})_{10}$] was prepared by dissolving 6.67 g at 70 °C in an aqueous solution during 3 h. The pH value of the micellar solution was adjusted with H_2SO_4 to 2.0. After homogenization, the solution was stirred during 3 h. Then the silica source, tetramethoxysilane (TMOS), was added drop by drop and the mixture was stirred again for 1 h. The surfactant/silicium molar ratio is fixed at 0.5 according to previous work [14,15]. The obtained gel was sealed in Teflon autoclaves and heated for 1 day at 80 °C. The final products were obtained after ethanol extraction with a Soxhlet apparatus during 30 h and calcination under nitrogen and then air atmosphere at 500 °C for 18 h to remove all the surfactant and impurities.

2.2. Structural and textural characterization

The X-ray diffractogram was recorded with a Panalytical X'Pert diffractometer equipped with a copper anode producing X-rays with a wavelength equal to 1.54178 Å. Nitrogen adsorption–desorption isotherms were carried out at –196 °C over a wide relative pressure range from 0.01 to 0.995 with a volumetric adsorption analyzer TRISTAR 3000 manufactured by Micromeritics. The sample was degassed further under vacuum for several hours at 320 °C before nitrogen adsorption measurements. The pore diameter and the pore size distribution were determined by the BJH (Barret, Joyner, Halenda) method [16]. The morphology of the obtained mesoporous materials was studied using a Philips XL-20 scanning electron microscope (SEM) with preparation of the sample by metallisation. The TEM micrographs were taken at 100 kV using a Philips Tecnai microscope. Sample powders were embedded in an epoxy resin and then sectioned with an ultramicrotome. The thin films were supported on copper grids previously coated by carbon to improve stability and reduce the accumulation of charges.

2.3. Photoluminescence study

The photoluminescence of the sample was excited by Hg lamp with the wavelength of 254 nm and detected by a cooled photomultiplier (Hamamatsu R943) linked to a grating monochromator.

3. Results and discussion

Fig. 1 gives the characterization results of our synthesized mesoporous material CMI-1 by different techniques. Three well-resolved peaks are seen in the X-ray diffractogram (Fig. 1A) which can be indexed on (100), (110) and (200) of a hexagonal symmetry. This is typical of a highly organized amorphous structure of silica with hexagonal arrangement of cylindrical channels. N_2 adsorption–desorption isotherm are of type IV, which is characteristic of mesoporous materials according to the BDDT classification [17]. The specific area by BET is very high up to 1019 m^2/g and the pore diameter distribution (insert of Fig. 1B) is quite narrow and approximately centred at 3.0 nm.

The highly ordered structure of the sample is confirmed by the TEM micrograph (Fig. 1C). The hexagonal arrangement of cylindrical channels is confirmed by the Fourier transform which shows a 6-fold symmetry (insert of Fig. 1C). The particles of the CMI-1 material studied by SEM (Fig. 1D) exhibit spherical and gyroïdal forms of 5–10 μm , typical morphology of mesoporous CMI-1 [14,15]. All the above observations show clearly that the synthesized material is made of hexagonally organized cylindrical channels with diameter of 3 nm.

The optical properties of the mesoporous material CMI-1 were studied by focusing on the photoluminescent behaviour of the sample. The corresponding PL spectrum is shown in Fig. 2A. Three PL bands, i.e., a very weak band near 2 eV (FWHM = 180 meV), a very intense blue band centered at 2.9 eV (FWHM = 620 meV) and another relatively intense UV band at around 3.9 eV (FWHM = 560 meV), are observed. The decomposition of the experimental spectrum in three Gaussian functions gives accurate values of these three observed PL bands.

The very weak band at 1.97 eV arises from the second-order diffraction of the UV band. Other than this artefact, no band can be observed in this region. However, a very intense band at 1.9 eV is always observed in amorphous silica, MCM-41 or MCM-48 photoluminescence spectra [13,18] and is attributed to non-bridging oxygen hole centers (NBOHC) ($\equiv\text{Si}-\text{O}^\bullet$) [7–12]. It is remarkable that this band is not observed in the silica matrix of our material CMI-1. This is quite interesting since the suppression of the band at 1.9 eV of silicas is a great challenge to prepare the advanced optical materials. The absence of this band in mesoporous CMI-1 silicas can shed some light on the design of such materials. The PL spectrum of the sample CMI-1 is only composed of two wide bands centred at 2.94 and 3.89 eV. According to Sakurai et al. [19] who

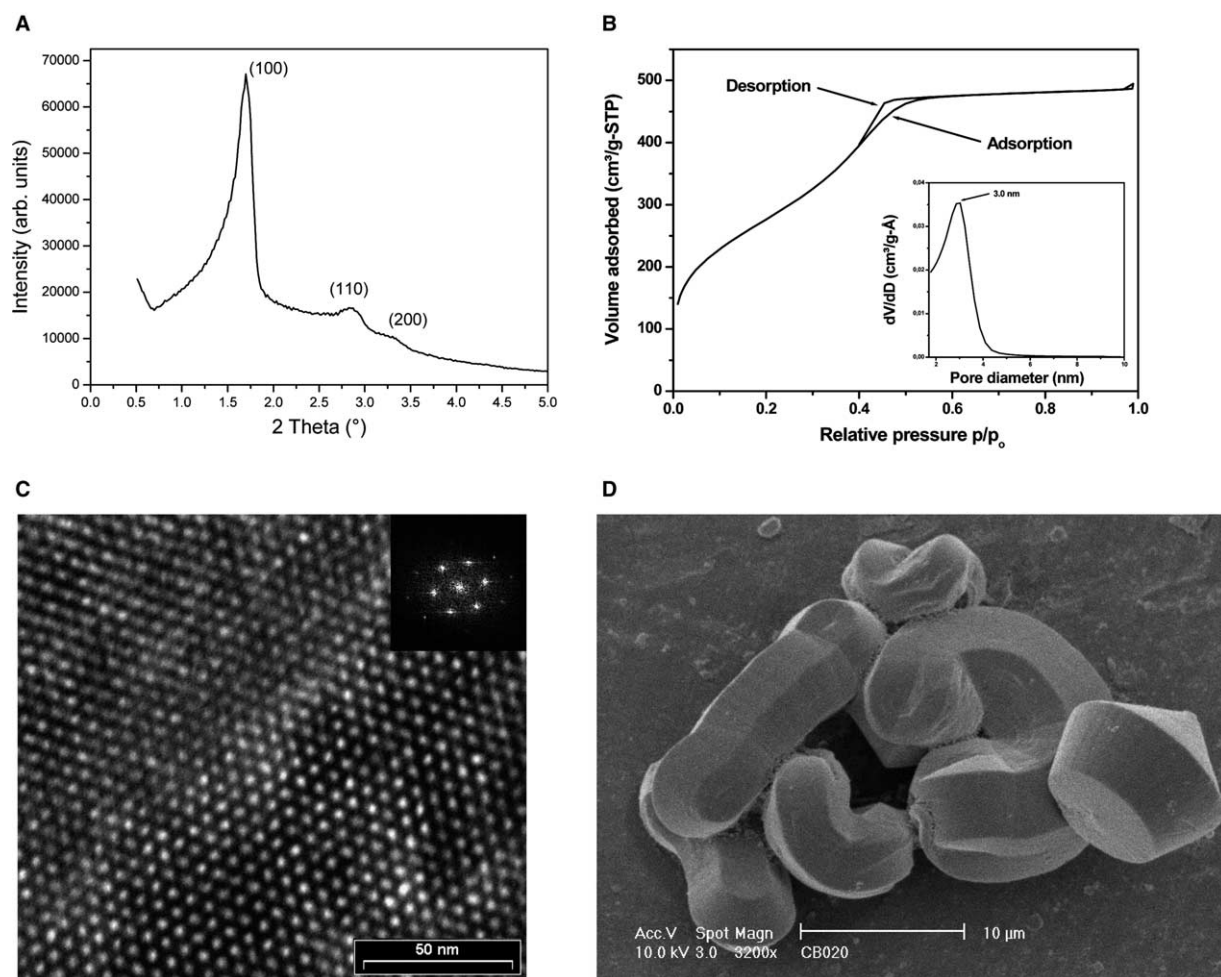


Fig. 1. Structural, textural and morphological characteristics of CMI-1 mesoporous materials. (A) Small-angle XRD pattern. (B) Nitrogen adsorption-desorption isotherm and pore size distribution (inset). (C) TEM micrographs and (D) SEM picture.

observed PL bands at 3.1 and 4.2 eV, these two bands could be generated by the great quantity of silanol groups present in the sample, whereas other scientists [20,21] believe that the photoluminescence is caused by defects like E' centers. In our sample, because of the extreme intensity of the band at 2.94 eV, we think that silanol groups inside the pore walls result in this photoluminescent emission. As to the band at 3.89 eV, its real origin is not clear yet, however, it is possible that this band have the same origin as that at 2.94 eV (see discussion below).

The absence of the 1.9 eV band can be explained by the use of a non-ionic surfactant during the synthesis of the mesoporous material CMI-1, which does not induce any electrical charge on the surface of the channels, in contrast to the synthesis of MCM-41 and MCM-48 materials which uses a cationic surfactant. A band at 1.9 eV was indeed observed in these two latter materials showing the existence of surface NBOHC type defects.

On the other hand, an ethanol extraction is used to eliminate surfactant molecules before the final calcination of our mesoporous material. This step allows the removal of a great amount of surfactant molecules and can avoid very

probably the local destruction of the material during the calcination. However, in the case of MCM-41, only a direct calcination was performed. The fast burning of the cationic surfactant molecules can create some surface defects which generate the photoluminescent emission at 1.9 eV.

In order to clarify the origin of the band at 3.89 eV, a CMI-1 sample was post-treated in water at room temperature during 2 h. After filtration, the water-treated CMI-1 sample was again calcined at 550 °C for 6 h. Its photoluminescence spectrum is shown in Fig. 2B. The second-order artefact of the band at 3.89 eV is still present near 1.9 eV. The intensity of the band at 3.89 eV which is slightly shifted toward higher energy is very strong and becomes dominant. It is possible that after this water post-treatment, the photoluminescent sites generating the emission at 2.94 eV are transformed to the sites giving the emission at 3.89 eV. This implies that the bands at 2.94 and 3.89 eV really come from the same origin. Indeed we consider, as other authors have proposed, that the band at 2.94 eV comes from the defect sites, such as E' centers ($\equiv\text{Si}^*$) while the band at 3.89 eV is due to defect sites of ($\equiv\text{Si}-\text{O}_2^*$) type.

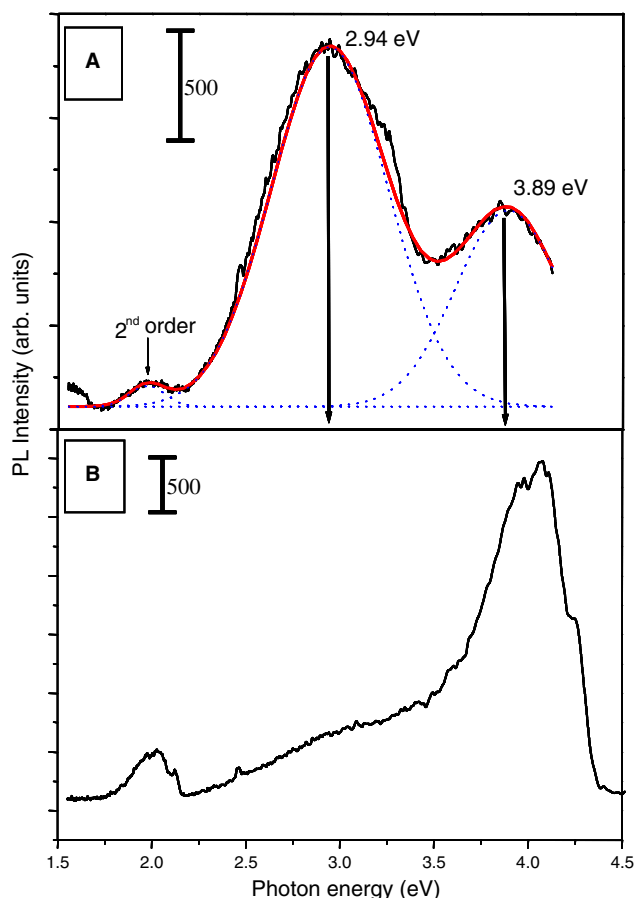
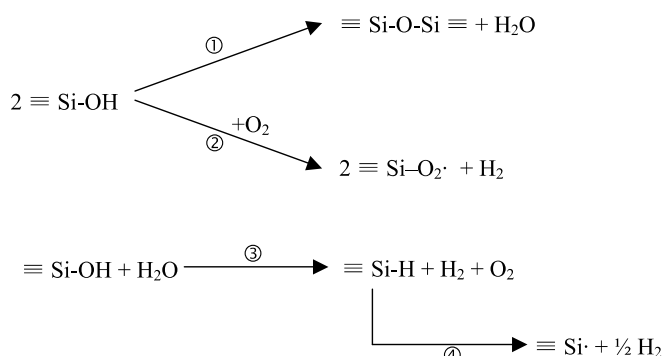


Fig. 2. Photoluminescence spectra ($\lambda = 254$ nm) of the mesoporous material CMI-1 with its Gaussian decomposition (A) and of water-treated the mesoporous material CMI-1 (B).

During calcination, the dehydroxylation mainly generates the siloxane ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) (route ①) (Scheme 1). The reaction ② can accidentally occur during calcinations in oxygen, giving $\equiv\text{Si}-\text{O}_2^\bullet$ (3.89 eV) defects. The E' centers can be generated by the reaction ③ and ④ as proposed by Kuzuu et al. [22]. The high intensity of the band at 2.94 eV in the CMI-1 sample suggests that the reactions ③ and ④ predominate. In this case, other than the formation of siloxane groups, silanol groups react with water molecules to give E' centers.



Scheme 1. Reaction routes generating different defect sites giving PL emission.

After water treatment of the CMI-1 sample, the silanol density sharply increases. The distance between two silanol groups is shortened. Two silanols can undergo a dehydrogenation reaction. Other than the main reaction ①, reaction ② is enhanced compared to reaction ③.

The above discussion suggests and confirms the hypothesis from literature that the bands at 2.94 and 3.89 eV are generated from the same origin, silanol groups. Depending on the treatment, E' centers ($\equiv\text{Si}^\bullet$) or $\equiv\text{Si}-\text{O}_2^\bullet$ defect sites can be produced in a relatively high quantity, explaining the changes in intensity of these two bands before and after water treatment.

4. Conclusions

The photoluminescent properties of a neutral surfactant templated highly ordered mesoporous silica CMI-1 sample are found to be quite different from those of MCM-41 material or silica glass. The absence of the 1.9 eV band indicates the absence of oxygen vacancies defects and non-bridging oxygen hole centers (NBOHC's) which were often observed in silica. A hypothesis concerning the origin of the band at 3.89 eV is proposed.

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